

AN INTRODUCTORY STUDY OF THE OXIDATION  
MECHANISM OF NICKEL

by

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## INTRODUCTION

Information such as the availability of and the rate of diffusion of metal ions, oxygen atoms, and electrons can be gained by establishing the oxidation rates of a metal under controlled conditions. Hedvall (15) and co-workers have shown a change in the oxidation rate in the region of the Curie temperature of nickel. Work cited by Lustman (22) showed a change in the oxidation rate of iron-nickel alloys in the temperature range 300 to 600° C. for the iron rich alloys and 400 to 600° C. for the nickel rich alloys. Lustman plotted the points of change in oxidation rates of the various compositions of the alloys on top of the iron-nickel phase diagram. He noted these points coincided with the transition regions from the ferromagnetic to paramagnetic state in the iron-nickel alloys. Lustman states that

Any change in the nature of the electron bond in the basis alloy that would bring about a change in the rate of formation of a reaction product film is not readily accounted for by the diffusion theory of film growth. It seems that a possible explanation would be based on some mechanism involving an electron transfer from metal to film.

All the theories that have been developed are based upon a diffusion mechanism (17,27,28,31,39,40).

Rideal and Wansborough-Jones (32) have suggested a relation between the activity of a surface and the ease of electron emission. An anomalous behavior in the thermionic and photoelectric emission of electrons from nickel in the region of the Curie temperature has been shown by Cardwell (2). This anomalous behavior of the electron emission and the oxidation rate leads

to the question; what role do the electrons play in the oxidation of nickel at this temperature? The study presented here is an introduction to a reconsideration of the oxidation rates of nickel and their relation to the availability of electrons in this region.

Nickel oxidizes to NiO in almost all cases and X-ray evidence suggests that this face-centered cubic oxide is the only stable structure (4,33). Electron diffraction and electron micrograph studies by Hickman and Gulbreensen (16) show that the oxide film formed on nickel is a stable adherent film of NiO with no lattice transformations between 400 and 900° C. Nickel atoms are found in the oxide to a considerable proportion under 400° C. (14,35) and the oxidation rate is very low in this region (43). The only data found for oxidation rates below 400° C. are given by Hedvall and co-workers (15). More and Lee (25), Tammann (36), Wagner (41), and others (5,21,39, 42) have studied the oxidation rates above 400° C. and all but Wagner and Tammann have observed a parabolic rate i.e., the thickness is proportional to the square root of the time. Tammann showed that the oxidation rates of some of the metals along with nickel follow an exponential function of the time,  $t = a \exp bx$  where  $t$  is the time,  $x$  is the thickness and  $a$  and  $b$  are constants. Workers using more precise methods than the optical method used by Tammann have also shown this law. However, this law has often been challenged and has no theoretical explanation (22). Wagner's studies were at 1000° C. and Krupkowski and Jazczurowski (21) found a parabolic rate for this temper-

ature. Early work on oxidation consisted of observing the relative ease of oxidation of different metals and the structure of the oxide (27,28).

To determine accurately the oxidation rate and thus the mechanism of oxidation, other than by trial and error, it is necessary to establish the precise mechanism by which the oxide films are formed. The processes employed for oxidation rate studies are reviewed in Jost (20) and consists of gravimetric, electrometric, volumetric, and optical methods. Of these methods, the gravimetric method as developed by Gulbransen (12) employing a vacuum microbalance has the most direct approach, with the least amount of assumptions, to the oxidation rates. The great sensitivity of this method was also deemed necessary for this problem, because of the low oxidation rate of nickel under 400° C.

#### PRELIMINARY STUDY

When a metal is heated in the presence of oxygen an oxide is formed at the surface. If the volume of a unit cell of the metal oxide is greater than the volume of the unit cell of the metal, the oxide is generally not porous so that continued oxidation is possible only if the metal and oxygen can diffuse through the oxide (31,40). If the rate of diffusion is slow, the rate of oxidation is controlled by the diffusion process (22,27,23,29,40) and can be calculated from the affinity of the reaction, electrical conductivity and transfer numbers (40). Pilling and Bedworth (31) first showed that the rate of diffus-

ion and thus the rate of oxidation is inversely proportional to the thickness of the oxide, which gives a parabolic rate law. However, in some cases the rate is controlled by reactions at the phase boundaries (10). Other complications arise for low temperature and thin films (9,13,28). Nickel oxidizes to form a compact oxide layer (35) and has oxide to metal volume ratio of 1.62 (34).

Wagner (39) has suggested that it is not the neutral atoms but the ions and electrons which diffuse through the oxide layer. This ion diffusion from the metal to the oxide air interface was proven in the case of iron by Pfeil (30) and Jette and Foote (18). Radioactive tracer studies have shown that the oxide film is formed by the addition of new layers on the oxide-air interface in the case of copper (1). The oxygen migrates through the oxide by a cation diffusion mechanism (29). The oxidation rate is dependent on pressure to the extent of whether or not there are enough oxygen atoms striking the surface to supply the necessary cation sites for a diffusion mechanism.

Theoretical considerations of Mott and Cabrera (28) show that for the case of nickel above  $400^{\circ}\text{C}$ , the oxidation rate should vary as the one-sixth power of the pressure. Wagner and Grunewald (42) have also suggested this relation and found the oxidation rate to vary, but the experiment did not offer conclusive evidence of a variation of this order. More and Lee (25) state that a pressure of 10 cm. of Hg. will supply more than the cation sites made available at the nickel oxide oxygen interface and therefore the rate of oxidation is insensitive



to pressure variations in this region.

The diffusion in the oxide is caused by slight deviations from the strict stoichiometrical composition (27,40). Nickel oxide contains a large amount of nickel atoms below  $400^{\circ}\text{C}$ . and therefore the concentration of metal is nearly uniform throughout the film leaving a very small concentration gradient to work a diffusion mechanism. It is believed that this is probably the reason why nickel oxidizes so slowly under  $400^{\circ}\text{C}$ . It might be interesting to study the effect of rediation, capable of ionizing the nickel atoms, on the oxidation rate under  $400^{\circ}\text{C}$ . to see if this would increase the oxidation rate. Studies of the this nature are cited by Mott and Cabrera (28) in the case of aluminium. The most intensive study of the oxidation of a metal has been conducted, on copper then iron and zinc or aluminium, in this order. Oxygen is soluble in the oxides of copper and iron while it is not dissolved by the oxides of zinc or aluminium (28). The oxidation of nickel is probably controlled by a cation diffusion mechanism in the region of 400 to  $900^{\circ}\text{C}$ . Because of the excess metal in the oxide under  $400^{\circ}\text{C}$ . the oxidation would probably follow the case of aluminium.

The most complete theoretical explanation of oxidation is given by Mott and Cabrera (28); however it fails to accomplish a complete explanation in some respects. All their laws for a compact film are derived from a diffusion process and a simple diffusion process probably will not explain the case of nickel under  $400^{\circ}\text{C}$ . Their laws have no temperature dependence for logarithmic growth rates. The effect of surface structure

and crystal orientation is only lightly touched upon and the theory says nothing about the electronic state of the base metal. The important part of their theory which applies to parabolic rates is given in an earlier paper by Mott (27). The pertinent part of this paper will be presented here.

If the oxide film is to grow, it is necessary for electrons as well as ions to move through the oxide layer. The electrons migrate through the film by: 1. Thermionic and photoelectric emission from the metal to the conduction band of the oxide, 2. "Positive" holes moving from oxide-gas interface inwards, 3. The quantum mechanical tunnel effect applicable only to very thin films. The work necessary to bring an electron from the metal to the oxide band will be less than that necessary to remove an electron from a clean surface in a vacuum (26).

The rate of growth of the film will be proportional to the number  $j$  of ions crossing unit area per unit time

$$\frac{dx}{dt} = j \Omega \quad . . . . 1$$

where  $\Omega$  is equal to the volume of oxide per metal ion. If the growth of the film is determined by the diffusion of ions and electrons from the metal to the oxygen-oxide interface, then  $j$  is determined by equations 2, 3, and 4 which follow

$$j = -D_i \frac{\partial n_i}{\partial x} + F n_i v_i \quad . . . . 2$$

Here  $n_i$  and  $n_e$  denote the concentrations of ions and electrons at a distance  $x$  from the metal oxide interface.  $D_i$ ,  $D_e$ ,  $v_i$ ,  $v_e$ , denote their respective diffusion coefficients and mobilities. The first equation gives the number of singly



charged ions and the second gives the number of electrons.

$F$ , is the electric field set up in the oxide which is determined by Poisson's equation

$$\frac{dF}{dx} = 4\pi(n_1 - n_0) e. \quad \dots 3$$

Similar equations may be written down when  $n_1$  and  $n_0$  refer to vacant lattice points or positive holes.

General solutions to these equations have not been obtained so we shall confine ourselves to limiting cases. Consider first the difference between thin films, in which the distribution of ions and electrons in the film may be calculated independently of each other, and thick films where the space charge set up if  $n_1$  and  $n_0$  are equal becomes important. An estimation of the film thickness  $x$  can be made where the space charges become important. This occurs as follows: A concentration  $n$  of ions having one sign will give a field, according to equation 3, having a maximum value of  $F = 4\pi nex$ . If this field is to have a negligible effect on diffusion in comparison with the concentration gradient, equation 3 must be

$$Fnv = 4\pi n^2 evx \ll D \frac{\partial n}{\partial x}.$$

Writing

$$\frac{\partial n}{\partial x} \sim \frac{n}{x} \quad \text{and} \quad \frac{v}{D} = \frac{e}{kT}$$

the Einstein relation between the mobility  $v$  and the diffusion coefficient  $D$  of a charged particle and with  $x \ll x_0$  this equation reduces to

$$x_0 = \sqrt{\frac{kT}{4\pi ne^2}} \quad \dots 4$$

An approximate value for films reaching  $10^{-4}$  cm. per hour was given as  $x_c \sim 3 \times 10^{-5}$  cm.

Consider the case of thin films where the electrons and ions pass from the metal to the oxide-oxygen interface. Denote by  $\phi$  the work required to bring an electron from the metal into the oxide, and by  $W$  the work required to bring a positive ion from the metal to an interstitial position in the oxide. Thus we may distinguish two cases:

1. The case where  $\phi < W$ . There will then be a uniform concentration of electrons in the oxide film and a concentration gradient of ions. If  $n(x)$  is the number of ions per unit volume at a distance  $x$  from the metal-ion interface, the flow of ions will be given by

$$j = -\frac{\partial n}{\partial x} D_1 \quad \dots \dots 5$$

The equation may be integrated subject to the conditions that  $n = 0$  at the oxide-oxygen interface and  $n = n_0$  at the metal oxide interface.  $n_0$  is the concentration of metal ions in the oxide in equilibrium with the metal and is given by

$$n_0 = N \exp\left(-\frac{W}{kT}\right)$$

where  $N$  is the number of interstitial positions per unit volume. We thus obtain

$$j = \frac{n_0 D_1}{x}$$

or from equation 1

$$\frac{dx}{dt} = \frac{n_0 \Omega D_1}{x}$$

whence

$$x^2 = K_1 t \quad \text{where} \quad K_1 = 2n_0 \Omega D_1$$

a parabolic law of growth is thus obtained for all thicknesses less than  $x_0$  with a rate constant  $K_1$  which increases rapidly with temperature.  $D_1$  is equal to  $b \exp(-U/kt)$ , the Arrhenius equation introduced into oxidation theory by Dunn (6), where  $U$  is the activation energy and  $b$  is a constant. We may take  $N\Omega \sim 1$ ,  $b \sim 10^{12} \text{ sec}^{-1} \times (10^{-8} \text{ cm})^2$  thus  $K_1 \sim 10^{-4} \exp(-(W + U)/kT) \text{ cm}^2/\text{sec}$ .

2. For the case where  $\phi > W$  Mott develops a logarithmic equation.

Gulbransen (13) obtains an equation from the transition state theory of Evans (8) and co-workers of the form

$$x^2 = 2 Dt + B$$

where

$$D = \lambda^2 \frac{kT}{h} \exp\left(-\frac{\Delta S}{R}\right) \exp\left(-\frac{\Delta H}{RT}\right)$$

where  $\lambda$  is the distance between successive interatomic sites,  $k$  is Boltzmann's constant,  $h$  is Planck's constant,  $B$  is an additive constant,  $R$  is the gas constant per mole where  $k = R/N_0$ ,  $N_0$  being the Avogadro number,  $\Delta S$  is the entropy of activation,  $\Delta H$  is the enthalpy of activation and  $D$  is the diffusion coefficient in transition state theory.

This is the equation we get from Mott's work if  $W$  is interpreted as  $\Delta G$  the Gibbs free energy of the activation process for constant temperature and pressure.

$$\Delta G_1 = \Delta H_1 - T \Delta S_1$$

we thus get

$$n_o = N \exp\left(-\frac{\Delta G_1}{RT}\right) = N \exp\left(-\frac{\Delta H_1}{RT}\right) \exp\left(\frac{\Delta S_1}{R}\right)$$

and if  $N\Omega = 1$  we get

$$K_1 = 2 \lambda^2 \frac{kT}{h} \exp\left(\frac{\Delta S_1 + \Delta S}{R}\right) \exp\left(-\frac{\Delta H - \Delta H_1}{RT}\right)$$

Since it is impossible to distinguish between  $\Delta S$  and  $\Delta S_1$  and  $\Delta H$  and  $\Delta H_1$  these quantities can be lumped together.

$\Delta H$  differs from  $U$  the activation energy, by  $P\Delta V$ , and since this quantity is small compared to  $\Delta H$  and  $U$  we can write

$$K_1 = 2 \lambda^2 \frac{kT}{h} \exp\left(\frac{\Delta S}{R}\right) \exp\left(-\frac{U}{RT}\right)$$

where  $U$  is now the activation energy per mole. This is the equation that More and Lee used in their study of nickel and cobalt. They found that the energy of activation was the same for these two metals, but that the oxidation of cobalt was twenty-five times faster than the oxidation of nickel due to the entropy factor. The difference in the entropy factor is attributed to there being twenty-five times more active surface sites on cobalt than on nickel. One could question this, however, upon grounds of difference in surface preparation of the two metals.

#### SYSTEM

The fundamental requirements of an oxidation system are the control of the composition and temperature of the oxidizing

atmosphere, the determination of the rate of oxidation, and the physical conditioning of the specimen. In an endeavor to satisfy these requirements a system was constructed as shown in Plate I and schematically in Plate II.

The oxidation atmosphere was controlled with a glass and metal vacuum system. The system is evacuated during the outgassing and preliminary heating period by a Cenco Hyvac mechanical forepump in series with a Distillation Products Incorporated MCF 300 fractionating pump. A pressure of less than  $10^{-5}$  mm of Hg. was obtained in our system during this outgassing period.

The pressures below  $10^{-3}$  mm of Hg. were determined by a D.P.I. VG-1A ionization gauge. A Pirani gauge was used to indicate when the fractionating pump could be operated and when the pressure was low enough to measure with the ionization gauge. A mercury manometer which was isolated from the rest of the system by an air trap surrounded by dry ice in acetone was used to measure the pressure at which the oxidation took place. The height of the mercury column was measured with a cathetometer.

The oxidizing atmosphere was pure dry oxygen obtained from heating potassium chlorate. The oxygen was dried by passing it over anhydrous phosphorus pentoxide which also removed the water vapor from the rest of the system.

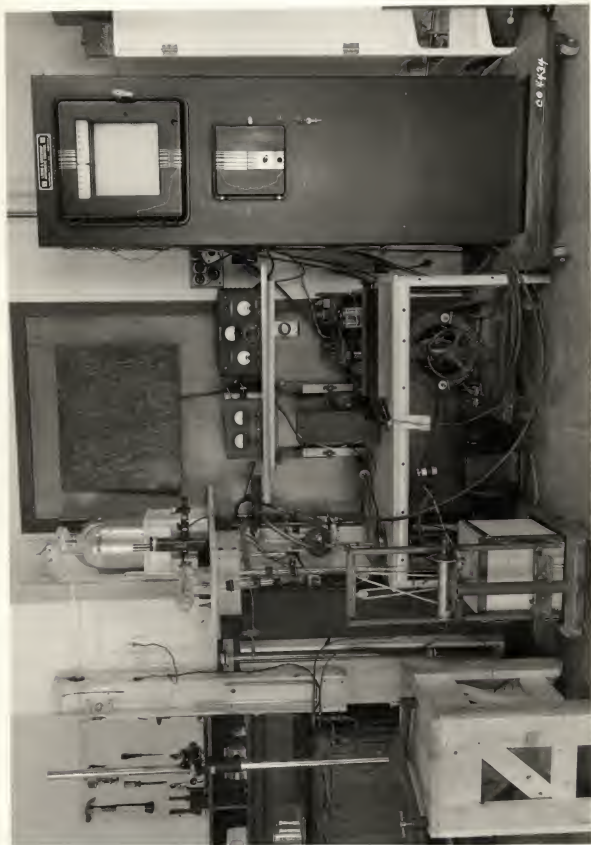
A furnace was constructed which could be moved up a vertical track to surround the quartz tube containing the specimen. The furnace was well insulated and capable of producing temperatures to  $1000^{\circ}$  C. The temperature of the furnace was controlled with a Leeds and Northrup Model S, 40,000 series recording

EXPLANATION OF PLATE I

The entire oxidation apparatus



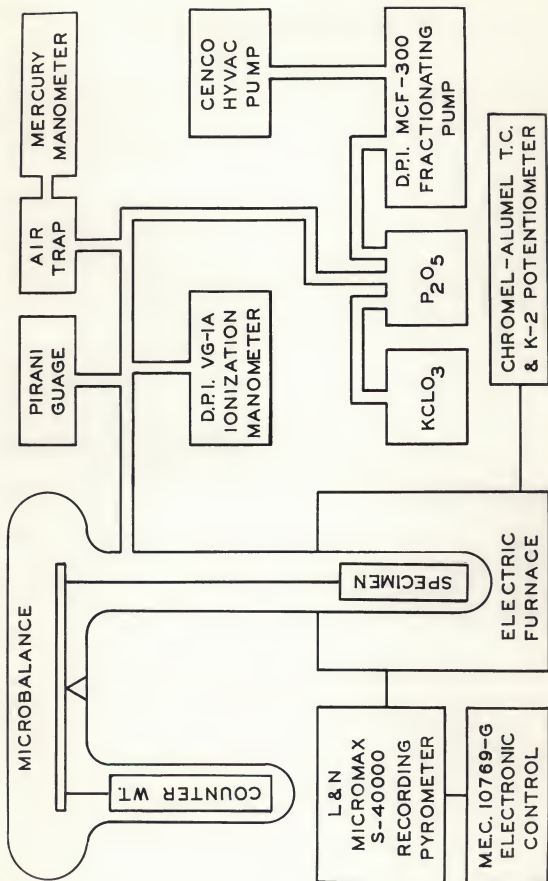
PLATE I



EXPLANATION OF PLATE II

Schematic diagram of the oxidation system

PLATE II



pyrometer and M.E.C. 10769-G electronic control unit. The temperature was checked by the Chromel P and Alumel thermocouple used by the control and a type K-2 Leeds and Northrup Potentiometer.

The actual temperature of the specimen was obtained at several temperatures by attaching a thermocouple to a dummy specimen in the system and simulating oxidation conditions. The difference in the two temperatures caused by the inhomogeneous character of the furnace was subtracted from the control temperature of the furnace. The thermocouples were checked against the tables at the ice point and the condensing vapor point of sulphur and found to be accurate to within one-half of a degree centigrade.

By running the line voltage to the electronic control through a constant voltage transformer and setting the furnace current with a large variac, the temperature remained constant to within plus or minus one degree centigrade of the control point over extended periods of time. Without the control it was observed that the temperature would randomly vary at the rate of about two and one-half degrees per hour.

The determination of the rate of oxidation was accomplished by actually measuring the weight of the oxygen taken up in forming the oxide. A quartz beam vacuum microbalance as shown in Plate III was constructed from the design of Gulbransen (13) and notes obtained from the National Bureau of Standards. The geometry of the balance was determined from the requirements of co-planar suspension and a desired sensitivity. The pivots of the balance were made from lengths of one mil annealed

EXPLANATION OF PLATE III

The quartz beam vacuum microbalance

## PLATE III





tungsten wire. Fused silver chloride was used to fasten the pivots to the beam and the quartz frame. The beam was selectively ground until it was in perfect balance on the central pivot, the suspensions were of equal weights of tungsten, and the specimen and counterweight were of equal weights of nickel so that the balance had perfect symmetry with respect to the central pivot. The symmetry in the construction of the balance provides a pressure and temperature sensitivity which is smaller than the sensitivity of the balance.

The measurements of the weight increase of the specimen were obtained from

$$\frac{\Delta d}{\Delta z} = \frac{l^2}{Gs}$$

where  $\Delta d$  is the deflection of the beam measured at the outer pivot point,  $\Delta z$  is the increase in weight,  $l$  is the length from the central pivot to the outer pivot,  $G$  is the weight of the beam, and  $s$  is the distance of the beams center of gravity from the pivot point. The deflection of the beam  $\Delta d$  was observed by a traveling microscope with a filar-micrometer eyepiece, which was calibrated against a standard ten millimeter scale. The co-planar suspension requires the three pivot points to lie in the same plane. Non-coplanar suspension would have the same effect on the sensitivity as an additive constant. The resisting moments of the pivots can be calculated to be small in comparison to the sensitivity of the balance. The difference in the density <sup>of oxygen</sup> around the counter-weight and the specimen varies the measured weight of the oxide by an amount cal-

culated to be less than ten micrograms under the most extreme temperature differences.

The sensitivity was determined from a set of calibration curves. A typical calibration curve is shown in Plate IV. The calibration curves were obtained by interchanging, from one end of the beam to the other end, wires of known weights and observing the deflection of the beam. The pans and wires used in calibrating the balance were of approximately the same weight as the specimen used. The wires used in measuring the sensitivity of the balance were calibrated by the author on the Department of Chemistry microbalance. Although the weights of the wires were not known to within five micrograms the difference in the weight of the wires was measured to within one or two micrograms. This was based upon the fact that the sensitivity of the chemistry microbalance was observed frequently during the weighing and remained constant. The wires were weighed upon two consecutive days and only the wires checking to within five micrograms were used in the calibration of the balance. By interchanging the calibrated wires and plotting the difference in weight against displacement of the beam a sensitivity of 0.0127 mm per microgram was obtained.

The physical conditions of the specimen will be discussed in the next section.

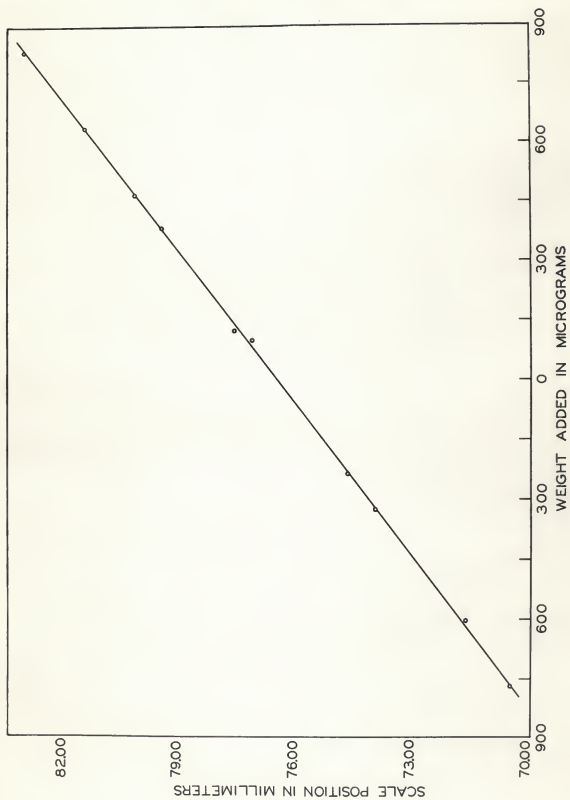
#### PROCEDURE

The nickel used in this study was obtained from the International Nickel Company in fifteen to eighteen thousandths of

EXPLANATION OF PLATE IV

Calibration curve for the quartz  
beam vacuum microbalance

PLATE IV



an inch thickness electro-deposited sheets. The impurities in the special electrolytic nickel were Co-0.043%, Fe-0.002%, Cu-0.005%, and Pb-0.0008%. X-ray transmission pictures showed that annealing for one hour at 900° C. was sufficient to remove the stress and preferred orientation produced by the most severe cold working of the nickel specimens. Prolonged heating above 900° C. produced large crystal growth while long periods of heating below 800° C. had no effect upon the crystal size or orientation (23). The bottom picture of Plate V shows the definite preferred orientation produced by rolling the nickel specimen while the top picture shows a uniform crystal size with no preferred orientation. The crystal size was estimated to be about 0.006 cm from considerations presented by Taylor (37) in his book on X-ray Metallography.

It was impossible to obtain a smooth surface because the specimens were too thin to be polished. The specimens were rough ground with number 240 crocus cloth and given an acid etch for one hour in an attempt to obtain an uniform surface preparation. The roughness factor i.e., the ratio of the true surface to the apparent surface of nickel may vary as much as 4 to 75 times depending upon the surface preparation (7).

The specimen used in any given oxidation run was prepared with a predetermined apparent surface area and a weight of 0.7 gram so that it would be in the calibrated range of the balance and give an easily observable deflection of the balance beam in one-half an hour during the oxidation run.

An oxidation run was started by placing the prepared speci-

# EXPLANATION OF PLATE V

X-ray transmission pictures of nickel

top: free lattice structure and small crystal size

bottom: stressed lattice structure with definite preferred  
orientation of the crystals



## PLATE V



men in suspension from the balance beam and filling the potassium chlorate, the phosphorus pentoxide containers, and putting dry ice around the air trap then pumping the system down to better than  $10^{-5}$  mm Hg. After the system was pumped down, the furnace was raised around the quartz tube containing the specimen and heated stepwise to  $700^{\circ}$  C. The temperature  $700^{\circ}$  C. was chosen because nickel has no crystal growth at that temperature. The vapor pressure of nickel below  $1000^{\circ}$  C. is very low so there is no observable weight change due to evaporation (19).

When the temperature had been at  $700^{\circ}$  C. for one hour, the temperature was returned to the control point of the chosen oxidation temperature. After one hour at the oxidation temperature, the system was shut off from the pumps and oxygen was applied by heating the potassium chlorate until a pressure of 10 cm Hg was reached. The pressure was controlled by further heating the potassium chlorate to increase the pressure or very briefly opening the system to the pump to reduce the pressure.

A scale reading was taken of the position of the reference point and balance beam position during the outgassing and as soon as possible after the oxygen was added. The rest of the run consisted of periodically taking readings of the balance beam position, the temperature, and the pressure.

To stop the oxidation run the furnace was lowered from around the specimen and the system was opened to the pumps. Any difference in reading of the beam position before the run was stopped and after the run stopped was subtracted from all the readings to correct for buoyancy and convection current

effects around the specimen.

A plot of the weight increase in micrograms per square centimeter against the time of oxidation was obtained from the beam position, the known sensitivity of the balance and the measured apparent area of the specimen. To find the value of  $K$  in the equation  $x^2 = Kt$  the value  $x^2$  was plotted against the oxidation time and  $K$  was calculated from the slope of the linear region of the curve. The value of  $U$ , the activation energy, was obtained from the equation  $K = 2 \lambda^2 kT/h \exp \Delta S/R \exp -U/RT$  by calculating the slope of the curve obtained by plotting  $\log K$  vs  $1/T$ .

No attempt was made to calculate  $\lambda^2$  or  $\Delta S$  because these quantities were not presented in the theory given by Mott (27) and multiple values of  $K$  were found at the lower temperatures.

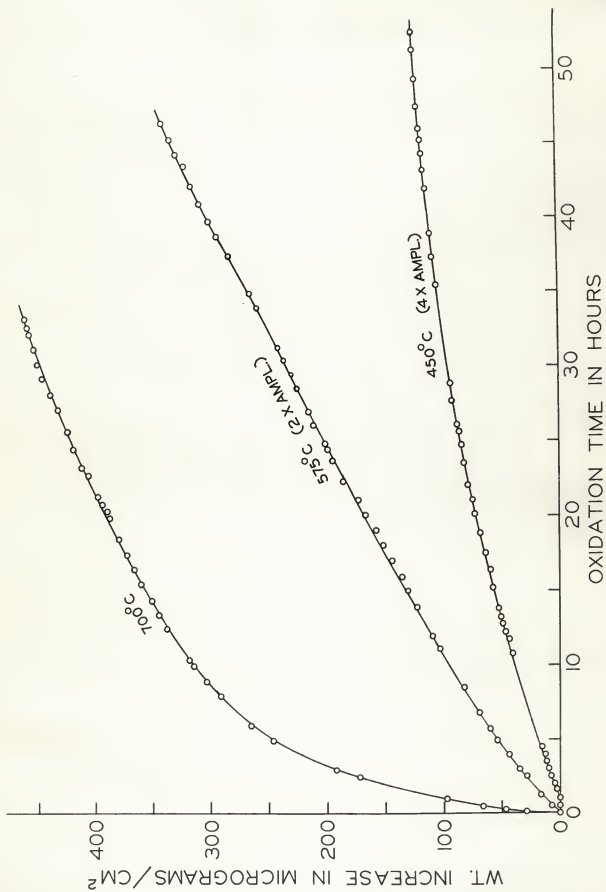
## RESULTS

A value for the activation energy of nickel of 30,400 calories per mole was obtained from the plot of  $\log K$  vs  $1/T$  shown in Plate VIII. The points above the line at the value 1.179 for  $1/T \times 10^3$  came from the fact that the 575° C. run never really reached the parabolic rate and there were three regions in which one could draw a straight line through the points on the square of the weight increase vs the time curve as shown in Plate VII. The greatest slope and the only straight line portion of this curve came from a slight hump in the 35 to 50 hour portion of the weight increase vs time curve as shown in Plate VI and probably should not be interpreted to mean

#### EXPLANATION OF PLATE VI

A plot of the weight increase in micrograms per square centimeters as a function of the oxidation time.

## PLATE VI

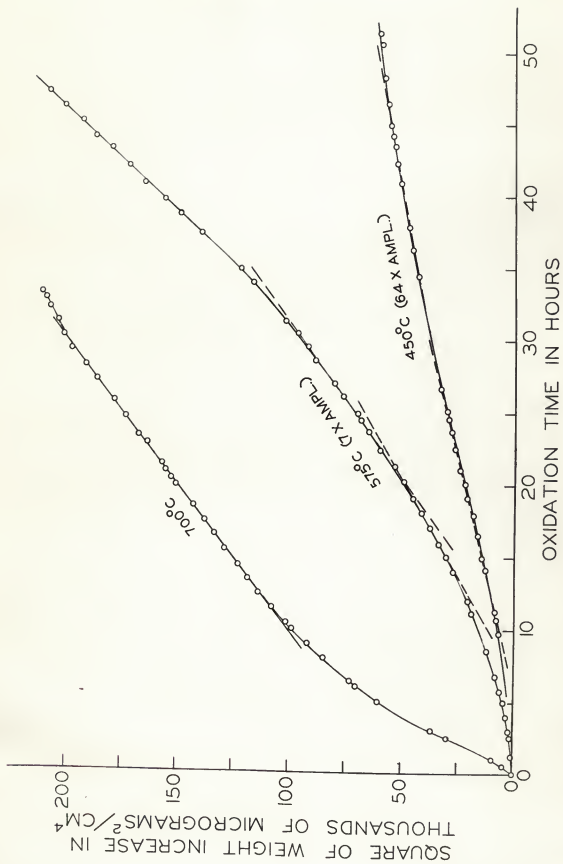


#### EXPLANATION OF PLATE VII

A plot of the square of the weight increase in micrograms squared per centimeter to the fourth power as a function of the oxidation time.



PLATE VII



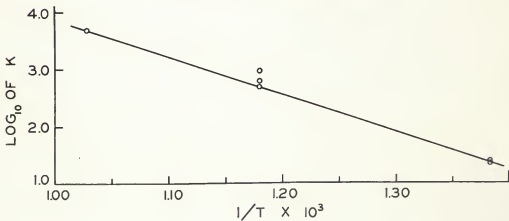
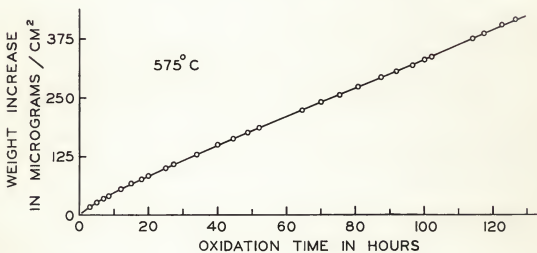
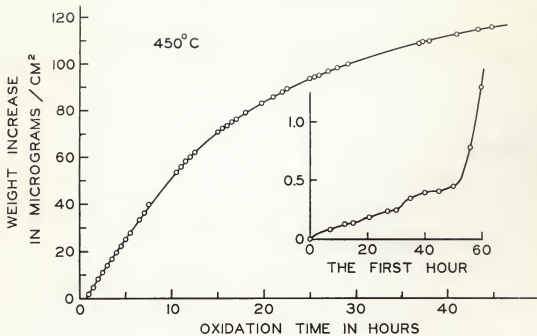
### EXPLANATION OF PLATE VIII

Top: A plot of the weight increase in micrograms per square centimeter as a function of the oxidation time which shows the anomalous initial oxidation rate at  $450^{\circ}\text{C}$ .

Middle: A plot of the weight increase in micrograms per square centimeter as a function of the oxidation time which shows the linear region in the oxidation rate at  $575^{\circ}\text{C}$ .

Bottom: A plot of  $\log K$  as a function of one over the absolute temperature.

## PLATE VIII



anything. The hump is small and is at the beginning of the linear region shown in Plate VIII for the  $575^{\circ}$  C. curve which would give the straight line portion on Plate VII. The two points at 1.38 for  $1/T \times 10^3$  are also caused by the oxidation rate never becoming a parabolic relation.

The plot of the weight increase of the oxide film per square centimeter as a function of time for  $450^{\circ}$  C. shown on Plate VIII demonstrates an anomalous oxidation rate during the first hour of oxidation as indicated on the insert on this plot. The anomalous initial oxidation rate was not observed for the  $575^{\circ}$  C. and  $700^{\circ}$  C. runs while it was observed for the  $450^{\circ}$  C. run shown in Plate VI. The slow initial rate was also observed for a trial run made at  $350^{\circ}$  C. to show that the oxidation rate was observable at that temperature. The anomalous effect might be explained if the oxide initially formed with a stressed nickel structure in the plane of the specimen surface and then after the first hour broke away to form its own free structure. Electron diffraction patterns were made from the nickel oxide which was formed during the entire  $450^{\circ}$  C. run and also of oxides formed in less than one hour at that temperature. All the patterns were found to be the pattern for nickel oxide with the only difference in the patterns being that the 400, 331, and 240 lines were more diffuse for the thin oxide films. A typical NiO electron diffraction pattern obtained for the thick oxide film is shown in Plate IX. Further study will have to be made on the electron diffraction patterns to ascertain whether there really is a change in the structure of the oxide.

EXPLANATION OF PLATE IX

Electron diffraction pattern of nickel oxide

## PLATE IX



The anomalous initial oxidation curve of nickel at temperatures below  $450^{\circ}$  C. has not been published. It seems explainable that it has not been published however since the methods used in previous oxidation studies of nickel were not sensitive enough to show this very small effect. There is a similarity between the shape of the  $450^{\circ}$  C. and  $575^{\circ}$  C. curves in Plate VI. The similarity is more apparent when one notes the slope of the curves as compared with the  $700^{\circ}$  C. curve in Plate VII. The  $450^{\circ}$  C. and  $575^{\circ}$  C. curves never reach a truly parabolic form and the  $575^{\circ}$  C. curve was actually linear after 50 hours as shown in Plate VIII. The anomalous initial rate and the deviation of the curves from a parabolic form suggest that the rate constant is a function of the film thickness. Mott and Cabrera (28) suggest a change in rate constant with film thickness. The very abrupt change after one hour in the initial rate at  $450^{\circ}$  C. and our not knowing the exact way the rate constants change with film thickness for our runs prevents us from making an easy interpretation of the exact change in the constants with film thickness as purposed by Mott and Cabrera. Further study of the theory in view of this changing rate with film thickness may explain why nickel oxidizes so slowly under  $400^{\circ}$  C.

The value of the activation energy of 30,400 calories per mole seems fairly reasonable since 21,710 calories per mole was published by Krupkowski and Jaszczurowski (21) and 22,240 by Valensi (38) while More and Lee (25) more recently reported a value of 38,400 calories per mole. More (24) had reported a value of 34,300 earlier. The value of the activation energy



will change with the purity of the nickel used, the value being lower for low-purity nickel (41).

#### FUTURE STUDIES

The study will be conducted with lower temperatures and the results given here will be re-checked. A more thorough study of the anomalous initial rate at temperatures  $450^{\circ}$  C. and lower should prove to be very important in the theory of formation of nickel oxide.

The furnace needs to be wound non-inductively to study the oxidation rate of nickel in the ferromagnetic state. The ground joints need to be removed from the balance chamber and the chamber should be isolated from the rest of the vacuum system by a liquid air trap.

#### SUMMARY

The development of an oxidation study of nickel was discussed by presenting the present theory of oxidation, the details of the method of study, and the results obtained showing the great sensitivity of the method used. The oxidation rate was studied by actually measuring the weight of the oxygen which combined with the nickel to form nickel oxide during the process of oxidation. The weight increase of the nickel specimen was measured by observing the beam deflection of a quartz beam vacuum microbalance built by the author in the laboratory. This balance has a sensitivity of 0.0127 mm per microgram. The great sensitivity of the method used was illustrated by the small

deviation of the data points from the oxidation curves and by the observation of an anomalous initial oxidation rate only 0.002 of the total oxidation at a temperature of  $450^{\circ}$  C. and lower. The value of 30,400 calories per mole for the activation energy seems to be a good value compared with the published values. The anomalous initial rate observed at  $350^{\circ}$  C. and  $450^{\circ}$  C. and the linear region in the  $575^{\circ}$  C. run should be important to advance the theory of the oxidation of metals.

The fact that the anomalous initial oxidation rate has not been observed for nickel seems justifiable since this is the first time this sensitive method has been used to study the oxidation rate of nickel.

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AN INTRODUCTORY STUDY OF THE OXIDATION  
MECHANISM OF NICKEL

by

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AN ABSTRACT OF A THESIS

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Information such as the availability of and the rate of diffusion of metal ions, oxygen atoms, and electrons can be gained by establishing the oxidation rates of a metal under controlled conditions. Investigators who have studied the oxidation rate of nickel have observed a parabolic rate for temperatures from  $400^{\circ}\text{C}.$  to  $900^{\circ}\text{C}.$  and a very low rate below  $400^{\circ}\text{C}.$  with an observable change in the rate of oxidation at  $360^{\circ}\text{C}.$ , the Curie temperature.

The present theory for the formation of an oxide film following the parabolic rate was presented. The problem of finding the mechanism by which nickel oxidizes was attacked by studying the rate of oxidation with the most sensitive method available at this time. To study the rate of oxidation a system which could be used to control the oxidizing atmosphere and which had a method of measuring the rate of oxidation was constructed.

To control the oxidizing atmosphere a glass and metal vacuum system was constructed which could be evacuated to a pressure of less than  $10^{-5}$  mm Hg. during the outgassing of the nickel specimen. The temperature of the atmosphere was controlled by an electric furnace. The furnace was controlled with a recording pyrometer with an electronic control unit and was constructed in such a way that it could be removed from the quartz tube containing the specimen. To measure the rate of oxidation a quartz beam vacuum microbalance was constructed with a sensitivity great enough to measure the weight increase of the nickel specimen as it combined with the oxygen to form a compact atomic layer of nickel oxide.

Nickel was found to have an anomalous initial oxidation rate for temperatures of  $450^{\circ}\text{C}$ . and lower. The oxidation rate deviated from the parabolic rate law for temperatures up to  $575^{\circ}\text{C}$ . The anomalous initial oxidation rate and the oxidation rate deviating from a parabolic law suggest that the rate constants are a function of the oxide film thickness. This behavior in the oxidation rate of nickel had not been reported in the literature and should be important in the theory of the oxidation of metals. It probably has not been reported because other methods for studying the oxidation rates of nickel are not as sensitive as this method. A value of the activation energy for nickel was calculated which seems to be a good value compared with the published ones.